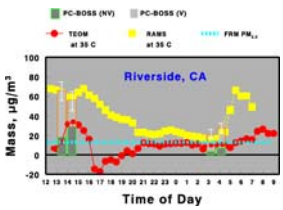
Encouraging Commercial Development of New Techniques for the Real-time Characterization of $PM_{2.5}$ Mass and Composition

William E. Wilson, U.S. Environmental Protection Agency, ORD/NCEA/NCEA-RTP, Research Triangle Park, NC;
Delbert J. Eatough, Brett D. Grover and Norman L. Eatough, Brigham Young University, Provo, UT

INTRODUCTION

Need: Automated monitors for particulate matter (PM) mass and components with 1-hour time resolution that accurately measure the PM that exists in the atmosphere and that people inhale.

Problem: Several existing techniques for 1-hour time resolution of PM mass must heat the collected PM to remove particle bound water. The heating evaporates semi-volatile ammonium nitrate and semi-volatile organic compounds as well as the particle bound water leading to an underestimate of the amount of PM mass that exists in the atmosphere and that people inhale. Semi-volatile components are also lost during collection of PM on filters due to pressure drop across the filter and during handling and equilibration to remove particle bound water. This problem is illustrated in the Figure to the right. Filter techniques for measuring the organic carbon (OC) component of PM also measure volatile organic compounds that adsorb on the filter, leading to an overestimate of OC.



The data shown in this Figure, based on studies in Riverside, CA, illustrate the correct measurement of $PM_{2.5}$ with the RAMS and PC-BOSS samplers developed at BYU (Eatough et al., 2003) and the lower results obtained with conventional FRM or heated TEOM monitors due to the loss of semi-volatile ammonium nitrate and organic material during collection of particles.

Approach: Develop research techniques that measure semi-volatile and nonvolatile PM mass and components; conduct field monitoring studies to demonstrate the importance of the semi-volatile components of PM; encourage industry to develop new techniques suitable for routine monitoring of the both semi-volatile and nonvolatile PM mass and components; conduct research monitoring programs that provide platforms for instruments developers to test, evaluate, and improve new techniques for monitoring semi-volatile and nonvolatile PM mass and components. Include sufficient measurements to obtain mass closure, i.e., demonstrate that the sum of the measured PM components equals the measured PM mass.

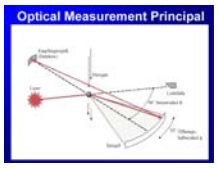
A major challenge in this effort is the development of techniques which accurately measure both the nonvolatile and semi-volatile (nitrate and organic material) fraction of $PM_{2.5}$ (Eatough et al. 2003). EPA and Brigham Young University have conducted cooperative research with industry to develop and/or test new techniques for measurements that include semi-volatile PM as well as nonvolatile PM. This research has lead to the identification of a suite of instruments with great promise for meeting this sampling objective with a significant reduction in the uncertainties associated with the measurement of semi-volatile fine particulate material. This has included working cooperatively with R&P Co. Inc. (Model 8500 FDMS TEOM Monitor) and GRIMM Technologies Inc. (Model 11101 PM Monitoring System) to demonstrate that the indicated instruments measure fine particulate mass, including the semi-volatile species (Grover et al, 2005a,b). Cooperative research with Sunset Laboratory (Dual Oven C Aerosol Analysis Field Instrument) and Dionex Inc. (ion-chromatography based gas and particle, GP-IC, monitor) has developed and/or validated new instruments which will measure carbonaceous material and inorganic composition in aerosols, including the accurate monitoring of semi-volatile organic material (Grover et al, 2005c) and ammonium nitrate (Grover et al., 2005b).

Rupprecht & Patashnick FDMS TEOM

The FDMS TEOM measures $PM_{2.5}$ mass, including semi-volatile ammonium nitrate and organic material, using a novel alternating measurement of mass with and without particle collection. The instrument has been validated in cooperative experiments between R&P, EPA and BYU in Rubidoux, CA (Grover et al., 2005a) and Fresno, CA (Grover et al., 2005b)

GRIMM Technologies PM Monitor

The GRIMM monitor measures $PM_{2.5}$ mass by the construction of particle size distribution data from measurements of individual particles by laser light scattering. The instrument has been demonstrated in joint research by GRIMM, EPA and BYU to measure total $PM_{2.5}$ mass including semi-volatile ammonium nitrate, organic material and particle bound water (Grover et al., 2004). In addition, the data obtained provide details of the accumulation mode particle size distribution.



Mention of trade names or commercial products does not constitute an endorsement or recommendation for use.

References

Eatough, D.J., Long, R.W., Modey, W.K., and Eatough, N.L. (2003). Semi-Volatile Secondary Organic Aerosol in Urban Atmospheres: Meeting a Measurement Challenge. *Atmos. Environ.* 37: 1277-1292.

Grover, B .D., Kleinman, M. A., Eatough, N. L., Eatough, D. J., Hopke, P. K., Long, R. W., Wilson, W. E., Meyer, M. B., and Ambs, J. L. (2005a). Measurement of Total $PM_{2.5}$ Mass (Nonvolatile plus Semi-Volatile) with the FDMS TEOM Monitor. *J. Geophysical Research*, in press.

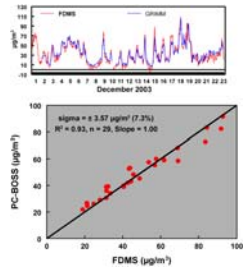
Grover, B.D., Eatough, N.L., Eatough, D.J., Ambs, J.L., Meyer, M.B., Hopke, P.K., Al-Horr, R., Later, D.W., Chow, J., Watson, J., and Wilson, W.E. (2005b). Measurement of Both Nonvolatile and Semi-Volatile Fractions of Fine Particulate Matter in Fresno, CA. Submitted to *Aerosol Science and Technology*.

Grover, B. D., Kleinman, M., Eatough, N.L., Eatough, D.J., Cary, R.A., Hopke, P.K., Smith, D., and Wilson W.E. (2005c). Measurement of $PM_{2.5}$ Nonvolatile and Semi-volatile Organic Material with the Sunset Laboratory Carbon Aerosol Monitor. Submitted to *J. Air & Waste Manage. Assoc.*

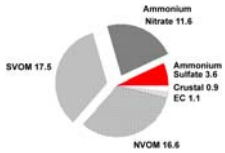
Grover, B.D., Eatough, N.L., Hopke, P.K., Wilson W.E. and Eatough, D.J. (2004). Measurement of Fine Particulate Mass, Including the Semi-volatile Constituents, with a GRIMM Monitor. *Proceedings, AWMA Symposium on Air Quality Measurement Methods and Technology,* April 19-22, 2004.

The top figure to the right illustrates the agreement between the FDMS TEOM and the GRIMM monitor in the Fresno study.

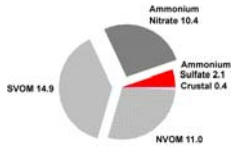
The data in the lower figure to the right illustrates the agreement between the R&P FDMS TEOM and the PC-BOSS, a denuder based integrated sampler (Eatough et al., 2003), in the measurement of $PM_{2.5}$ in Fresno, CA.



The ability of the FDMS and GRIMM to monitor the semi-volatile material in these aerosols is illustrated by the particle composition of the aerosols given in the two charts below. Note the large amount of semi-volatile organic material (SVOM) and ammonium nitrate present as well as nonvolatile organic material (NVOM).



Rubidoux



Fresno

DIONEX GP-IC

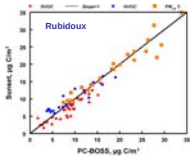
Dionex has developed an ion chromatographic instrument for the measurement of both gas and particulate phase ionic components. In cooperation with EPA and BYU, the instrument was first field tested in the experiment in Fresno, CA where particulate phase sulfate, nitrate, ammonium and other ions were monitored (Grover et at., 2005b). The Dionex results were in agreement with PC-BOSS data.

Sunset Dual Oven Ambient Carbon Monitor

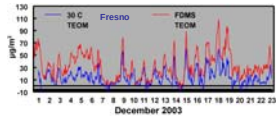
Joint research between Sunset Laboratory, EPA and BYU at Rubidoux, CA has shown that the Sunset Monitor shown to the left can be modified to allow for the determination of both nonvolatile and semi-volatile organic material in $PM_{2.5}$. Agreement between the dual oven approach and PC-BOSS results for nonvolatile organic material, semi-volatile organic material and total carbonaceous material are shown in the graph below (Grover et al., 2005a).

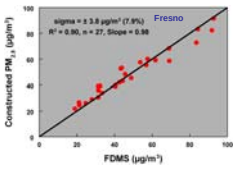
Closure Between Measured and Constructed $PM_{2.5}$ Mass

Use of the instruments described in this poster allows for the semi-continuous measurement of both $PM_{2.5}$ mass and components. The agreement that can be obtained between $PM_{2.5}$ mass measured with the FDMS TEOM and the $PM_{2.5}$ mass calculated from the measured components for 1-h average measurements is illustrated in the graph below to the left for the Fresno study. In contrast, a conventional heated TEOM monitor also loses semi-volatile material (shown for the Fresno study, below to the right), and the conventional EPA single filter FRM sampler measures the $PM_{2.5}$ mass retained on the filter but underestimates the $PM_{2.5}$ mass present in the atmosphere (shown below for the Rubidoux study, bottom right).

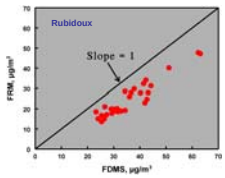


A Conventional TEOM Monitor Does Not Measure the Semi-volatile PM Detected by the FDMS TEOM





Closure Between Mass & Components Including Semi-volatile Components



The FRM Underestimates $PM_{2.5}$ Present in the Atmosphere